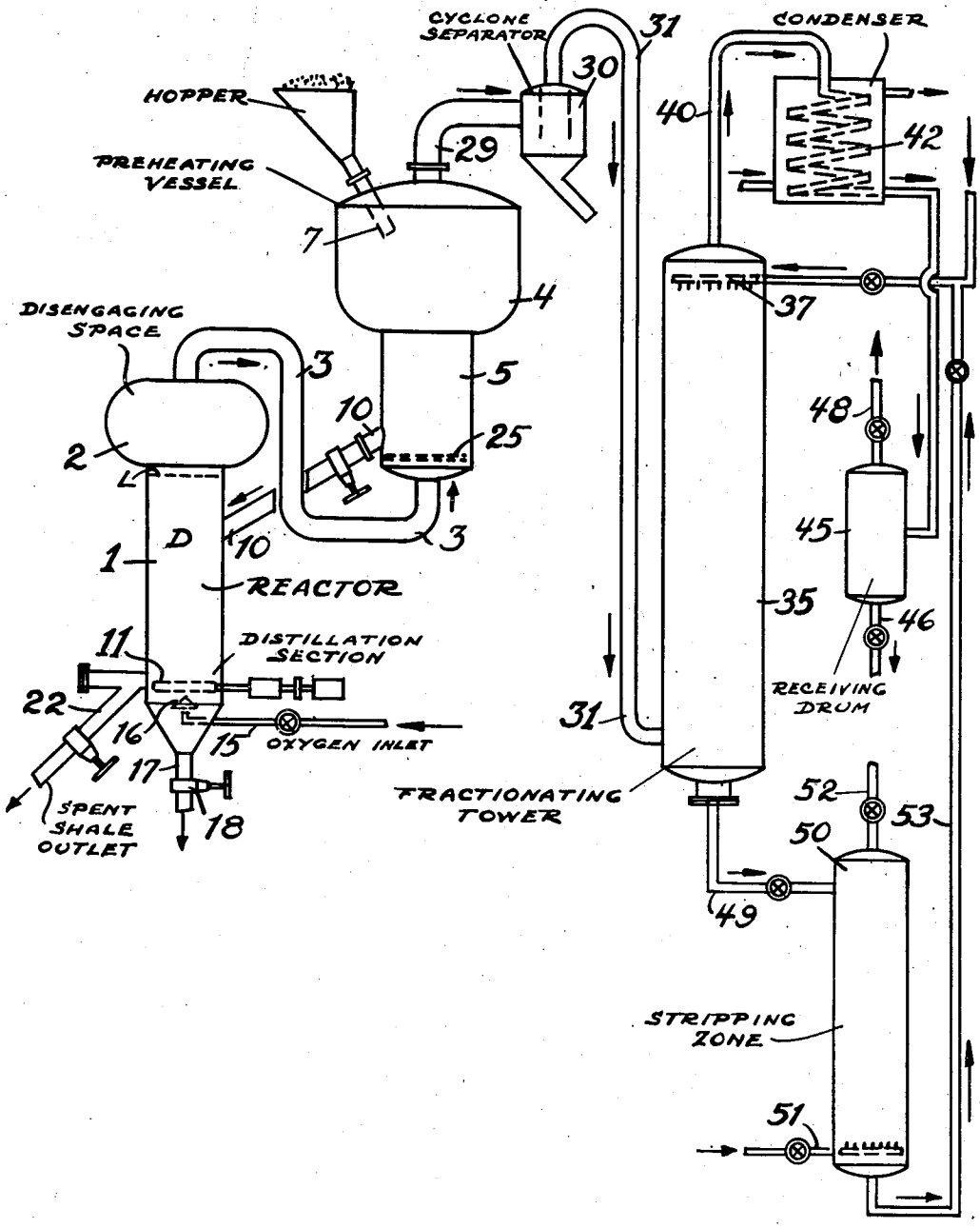
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FLUIDIZED SHALE AUTOTHERMIC DISTILLATION

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FLUIDIZED SHALE AUTOTHERMIC DISTILLATION

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The present invention relates to improvements in the art of producing oil from minerals, such as shale, oil sands, and the like, and more particularly it has to do with a continuous operation in which the shale or other oil-bearing mineral is fed to the reaction zone in the form of coarse lumps and there treated under temperature conditions sufficiently high to cause liberation of oil, the process also being characterized by the fact that the products of distillation and/or combustion are employed to preheat the shale in a zone prior to their introduction into the reaction zone.

Prior to our invention, shale and other oil-bearing minerals have been treated by allowing lumps of the material to fall through a shaft wherein they are treated with hot gases in which case the efficiency is very low because of the poor heat transfer between the gas and the rather large particles. More recently, processes have been developed in which shale is fed to a reaction zone in the form of powdered material and is subjected to thermal treatment with gases which are flowed at velocities such that the powdered shale is "fluidized," that is, the powder-gas mixture takes on the properties of a true fluid. The first process is inefficient, as stated, and has the further disadvantage that the coarse particles which are rich in oil, agglomerate as the pass through a high temperature zone and tend to plug the retort. The second operation, on the other hand, has the objection that fine grinding of the shale to produce powder is an expensive operation. Our process overcomes the disadvantages of the first type without the necessity of the expensive fine grinding used in the second. By taking advantage of the fact that coarsely ground material can also be "fluidized" i. e. given fluidity by treatment with a moving gas, so that the solid and gas together possess the flow characteristics of a liquid, our process is designed to utilize the sensible heat of a vaporous gas in heat exchange relation with fluidized solid particles under such conditions that the fluidized solid is not allowed to drop in temperature below the dew point of the vaporous gas. Agglomeration is further prevented by mixing finely powdered spent shale with the freshly ground shale particles in the preheating zone whereby the latter are prevented from adhering together or lumping by a surface covering of said fine dry material.

According to our process, we roughly grind shale to a maximum particle size of about ¼ to ½ in. in diameter. The roughly ground particles are then fed into a preheating zone where they are fluidized and heated by gases obtained in the

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subsequent distillation of the shale. The heating gases also contain finely divided particles of spent shale from the distillation and it is desirable that some of these particles remain in the gases when they are mixed with the fresh shale so as to prevent the freshly ground shale particles from agglomerating. The fluidized mass of shale is then fed into a reaction zone or retort where, under the influence of heat, the shale physically disintegrates into particles of powder size by release or decomposition of the agglutinants in the shale during the heat treatment having the attendant advantage of increased surface which facilitates release of the hydrocarbons from the shale.

It is the main object of our present invention, therefore, to subject raw shale to a continuous thermal treatment operation in a process under conditions which facilitate the handling of the shale and which is considerably cheaper and more expeditious than prior processes.

For illustration, one concrete embodiment of this invention is shown in the somewhat diagrammatic flow chart comprising the single view of the accompanying drawing.

In the drawing, 1 refers to a reactor which is a vertical, cylindrical vessel, expanded in its upper portion into a disengaging space 2 of greater diameter than the lower or distillation space D. Other dust separators may be used for further separation of solids and gases are desired but it is part of this invention to let some fine solids through to the preheater. A preheating vessel 4, into which roughly ground shale having a particle size of about ¼ to ½ in. is discharged through a feed inlet 7, is in communication with reactor 1 through a pipe 10, thus providing conduit means for transferring preheated shale from preheater 4 into the reactor 1. In operating the process, the roughly ground shale is introduced as stated through feed pipe 7 into preheater 4 where it is instantly preheated by hot gases and vapors (hereinafter identified) which are withdrawn from reactor 1 through line 3, and charged into section 5 forming the bottom of preheater 4 and thereafter forced upwardly therethrough. These gases have a temperature of 800–1000° F., depending on the type of shale treated and contain products of distillation of the shale, together with the flue gases that have been generated from burning spent shale or burning a gas in the reactor. In the preheater 4 the hot gases give up at least a part of their heat to the body of shale and increase the temperature thereof to about 400° to 600° F. It is important that the

temperature be maintained above the dew point of the gases and vapors to prevent condensation in the lower portion of vessel 5. At the same time that the gases serve to preheat the incoming shale they act as a fluidizing medium for the shale in the lower portion 5 of the preheater 4. This is accomplished by imparting velocities of from 2 to about 10 ft. per second to the gases entering the lower portion 5 of the preheater. This results in the formation of an ebullient mass of shale and gas having a level near the top of portion 5 of the preheater. Thus, an intimate mixing of all portions of the mass of shale is obtained so that the shale instantly acquires the average temperature of the whole mass. It is recognized that the substantially uniform temperature prevailing in the mass does not penetrate the larger particles instantaneously and it is therefore necessary to provide a residence time for the particles in the preheater which is great enough to allow the heat to penetrate the particles. There must also be a sufficient mass of material in the preheater so that it acts as a heat reservoir that does not suffer any substantial fluctuation in temperature as the fresh shale is added. It is found that a body of shale equal to a residence time of 2 to 10 minutes is satisfactory as a temperature reservoir and serves to give smooth operation. From the preheater the preheated shale flows as stated through line 10 into reactor 1 where a fluidizing condition is also maintained by an oxidizing gas such as air or oxygen, fed through line 15. The oxygen combines with the fixed carbon or other combustible material of the spent shale under combustion conditions to liberate the heat required for the reaction. Of course, the amount of oxygen is limited so as to burn only that amount of fixed carbon and other combustibles in the shale which will heat the mass to the desired temperature. In this reactor there is held a large mass of spent shale compared to the fresh shale added to maintain a heat reservoir, allow residence time for complete distillation of the shale, and minimize the combustion of oil products or the fresh shale.

In the reaction zone 1, the shale undergoes chemical conversion of certain natural constituents therein to hydrocarbons including gasoline and gas oil. These hydrocarbons are formed from an ingredient of the shale called kerogen, a substance containing nitrogen and sulfur, usually, as well as hydrogen and carbon. Hence, the heat treatment of the shale involves more than a mere distillation and for that reason best results require appreciable residence time of the shale in the reactor, say from 5 to 20 minutes. The chemical conversion of the kerogen in the shale to hydrocarbons and other products such as ammonia, hydrogen sulfide, etc., and their release from the shale by the thermal treatment, leave a residue of inert shale containing combustibles in the form of carbonaceous material or fixed carbon which is burnt in reactor 1, thus releasing heat in situ which is available for use in other portions of the process. The gas velocity that is the net velocity of the gas in the reactor, is from 2 to 10 feet per second, and under the conditions stated the shale will be in the form of a fluidized mass, i. e. an ebullient, turbulent mixture of solids in gas and vapors, having an upper level at about the line indicated by (L). Above (L) in disengaging space 2 of greater diameter than the reactor, the drop in the linear velocity of the gaseous material causes the larger particles of the shale which pass into the disengaging space to gravitate into the reactor 1.

Spent and burnt shale is withdrawn from the reactor through draw-off pipe 22. Since there is always a certain amount of non-combustible material in the shale fed to the reactor, slag is inevitably formed. This is continuously collected on rotating grate 11 and also withdrawn through outlet 22. It is preferable to provide the rotating grate with a scraper (not shown) or other mechanical device to draw the slag which accumulates thereon toward the draw-off pipe 22 so that it may be removed from the system. Any material which falls below grate 11 may be withdrawn through line 17 controlled by sliding valve 18.

A portion of the shale in reactor 1 is disintegrated to a powder having a particle size about 200 mesh or less. These fine particles do not drop out in the disengaging section 2 but are entrained by the gases removed overhead through line 3 and are conveyed along with the gases to lower portion 5 of preheater 4 where they serve to coat the particles of fresh shale therein and prevent them from agglomerating or lumping. The bottom of section 5 of the preheater 4 is provided with a foraminous member, such as a grid plate 25, through which the entering gases pass.

After the gases containing the products of combustion, as well as the hydrocarbon products of conversion, pass through the mass of roughly ground shale in preheater 4, they are withdrawn through line 29, passed through the dust separator 30, and then are discharged through line 31 into a quench tower 35 where they are cooled by oil sprayed into said tower by spray nozzle 37 as shown. From the tower 35, a heated gaseous fraction containing carbon dioxide, steam or water vapor and normally gaseous hydrocarbons are recovered through a line 40 and condensed in a coil 42 and thence passed into a receiving drum 45 from which the water may be withdrawn through line 46 while the normally gaseous material, that is the carbon dioxide and the hydrocarbons may be withdrawn through line 48. The hydrocarbons may be scrubbed out of the material in line 48 by suitable scrubbing means not described, to recover isobutanes, butylenes, propylenes, ethylene, ethane, methane, and the like.

The quench oil introduced through line 37 absorbs all of the heavier boiling material and is withdrawn through line 49. The fat oil thus obtained is then introduced into stripping tower 50 where it is contacted with live steam introduced through line 51. In this manner a fraction boiling within the motor fuel range is removed overhead through line 52, while heavier oil is withdrawn through line 53 and recycled to line 37 for use as quench oil introduced into the top of tower 35.

The disposition of the various hydrocarbons produced according to our shale distillation process are numerous, and it will be quite impossible, and in fact, it is entirely unnecessary, to describe in detail the method of processing the various products in order to obtain desirable products. The gasoline produced according to the method which we have described is not generally of high octane number, and obviously if this material is to be used as aviation gasoline, it will have to be hydroformed or otherwise treated to improve its octane number and then blended with alkylates and/or aromatics together with lead tetraethyl to form a finished aviation gasoline of good quality. The normally gaseous hydrocarbons may be

alkylated or dehydrogenated to form intermediates in the manufacture of synthetic rubber, rubber substitutes, and the like. The expert in the art will understand the numerous possibilities of refining or further processing products from the shale distillation operation to produce petroleum products of desired properties.

According to our process, we roughly grind shale to sizes varying approximately from pea to hazel nut size, and then feed this material into a body of already heated similar material in a preheater where there is a current of hot gases and vapors with a vertical velocity sufficient to "fluidize" the particles and instantaneously heat them to a temperature above the dew point of the gases and vapors where moisture is driven off without substantial vaporization of any oil from the shale. This instantaneous heating has a pronounced effect on the economy of the operation because it permits using the gases and vapors from the reactor to preheat the solids without condensing oil on the fresh shale and with minimum dilution of the oil vapors with flue gases or other heat carrying gases. From the preheater the solid particles flow to a reaction vessel where the hotter gases have a vertical velocity sufficient to "fluidize" the solid particles and instantly heat them to the reaction temperature of 800–1000° F. In the reactor the rough ground particles are largely disintegrated to smaller sizes which has several desirable effects, among which are, more uniform fluidizing, more rapid reaction and more complete reaction, resulting in better yields of oil. Finally, this disintegration produces a fine dry powder or dust part of which flows with the gases from the reactor to the preheater where it coats the particles that may have any tendency to agglutinate. Gangue brought in with the shale may not disintegrate into fine particles and, therefore, sinks to the grate 11 in 1 and is drawn off by known means such as a rotating grate.

The gist of our invention resides in the method of preheating and distilling the shale characterized also by the feature that the shale fed to the process is not finely ground but rather is roughly ground to the size that would be produced by running it once through an ordinary jaw crusher. By using this material as a feed stock we greatly reduce the operating costs. Also, in our process we preheat the shale in a preheater where it is subjected to the influence of the products of distillation and combustion originating in the reactor. In the reactor itself the shale undergoing distillation and combustion has been disintegrated to finely divided condition by decomposition of the natural agglutinants of the shale in the heat treatment. We prefer to operate our process so that the shale is burnt in the lower portion of the reactor using substantially pure oxygen. By operating in this manner it is not necessary to fractionate out of the products large quantities of nitrogen, as where air is used in regeneration. It is obvious that the quantity of oxygen discharged into the reactor must be carefully controlled so that the oxygen is substantially consumed and disappears in the lower portion of the reactor. The amount necessary in any given case will, of course, have to be determined beforehand. However, the step of preheating the shale by the hot gases from the distillation will save in the neighborhood of about one third of the amount of oxygen normally used. Burning of the spent shale in the lower portion of the reactor supplies a substantial quantity of the heat necessary to maintain the reaction, and due to

the fact that the shale in the reaction zone is in a turbulent, ebullient state the process is very flexible and accurate heat control is possible since virtually all portions of the mass of shale in the reaction zone are of the same temperature. The entering shale which is in the form of rather large lumps quickly disintegrates as it enters the reactor, into particles of powder size, due to the fact that the hot shale and hot gases cause decomposition of the aggultinants or adhesive material present in the raw shale. When operating at its best, and since the hydrocarbons are formed from kerogen, an oxygenated derivative of hydrocarbons, we maintain the shale in the reaction zone for a period of from 5–20 minutes depending on the ease with which the particles disintegrate to fine powder and thus allow the heat to permeate the shale. Since the capacity of any plant is largely governed by this resistance time, we may elect to operate with a high throughput which requires a short residence time. This may be achieved by finer initial grinding of the shale, higher reaction temperature with attendant sacrifice in the yield of oil. The residence time can be controlled by controlling the feed rates and the rate of draw-off.

Many modifications of our invention will readily suggest themselves to those who are familiar with this art.

What we claim is:

1. In the continuous distillation of oil-bearing shale, the improvement which comprises charging oil-bearing shale particles of about ¼ to ½-inch size to a preheating zone, flowing a mixture of hot combustion gases with hydrocarbon vapors from shale oil carrying in suspension dry shale powder into contact with said shale particles in the preheating zone, said mixture having substantially an oil shale distillation temperature, fluidizing and heating said shale particles in said preheating zone by said mixture to above the condensation temperature of the vapors, feeding the preheated shale particles into a separate distillation zone wherein they form a fluidized mass having an upper level, flowing hot combustion gases up through said fluidized mass at an oil shale distillation temperature to form the hydrocarbon vapors and disintegrate shale particles in the fluidized mass to dry shale powder, burning said spent shale particles with oxygen in the lower portion of said distillation zone to form the hot combustion gases flowing up through the fluidized mass, disengaging hot combustion gases mixed with the hydrocarbon vapors and dry shale powder formed in the fluidized mass from oil-bearing shale particles at above said upper level of the fluidized mass to form said mixture flowing into the preheating zone, and withdrawing vapors and gases from said preheating zone.

2. In the continuous distillation of shale, the improvement which comprises charging roughly ground shale to a preheating zone, passing hot combustion gases and distillation vapors from a subsequent distillation of the shale upwardly through the roughly ground shale in the preheating zone at a temperature substantially above the dew point of the distillation vapors, to fluidize and preheat the shale in said preheating zone by said combustion gases and distillation vapors to a temperature above the dew point of said distillation vapors, withdrawing the fluidized preheated shale from the preheating zone, discharging it into a separate distillation zone, flowing combustion gases upwardly through said distillation zone at a net linear velocity such that the shale is in

the form of a turbulent, ebullient mass of fluidized material, and at a shale distillation temperature causing physical disintegration of the shale into dry powder and spent shale with the formation of hydrocarbon vapors, forcing a gas containing oxygen through the lower portion of said distillation zone to cause combustion of spent shale in said lower portion, recovering gaseous material containing some of the dry powder from the upper portion of said distillation zone for discharge into said preheating zone and recovering vapors and gases containing gasoline and gas oil from said preheating zone.

3. The process of claim 2 in which said shale distillation temperature is about 800° to 1000° F. and the shale is preheated in said preheating zone to a temperature of about 400° to 600° F.

4. The process of claim 2 in which the roughly ground shale has a residence time in said preheating zone of about 2 to 10 minutes.

5. The method of distilling shale which comprises feeding roughly ground shale preheated in a preheating zone into a separate distillation zone, subjecting spent shale to combustion in a burning zone forming the lower portion of said distillation zone, passing hot combustion gases from said burning zone upwardly through said distillation zone to supply heat of distillation, controlling the net linear velocity of gases in said burning and distillation zones within the limits of 2 to 10 ft. per second so as to form a fluidized mass of shale particles having a level, maintaining the shale resident in the distillation zone for a period of from 5 to 20 minutes at a temperature in the range of from about 800° to 1000° F. whereby shale constituents are converted to hydrocarbon vapors of gasoline boiling range separating from undistilled shale, then passing said hydrocarbon vapors with gaseous products of combustion substantially at said temperature through the roughly ground shale being preheated in said shale preheating zone, preheating the shale in said preheating zone by said hydrocarbon vapors and gaseous combustion products to a temperature above the dew point of said hydrocarbon vapors, and recovering the vapors from said preheating zone.

6. The process of claim 5 wherein the shale has a residence time in said preheating zone of about 2 to 10 minutes.

7. Method set forth in claim 2 in which the linear velocity of the gases in the distillation zone is maintained within from 2–8 ft. per second.

8. The method of claim 2 in which the shale is maintained in the distillation zone for a period of from 5–20 minutes.

9. Process according to claim 5 in which the velocity of the vapors and gaseous products conveyed to said preheating zone is maintained between 2 and 10 feet per second so as to fluidize shale particles in said preheating zone and maintain the temperature therein above the dew point of the hydrocarbon vapors.

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